

B3

(19)		Canadian Intellectual Property Office An Agency of Industry Canada	Office de la Propriété Intellectuelle du Canada Un organisme d'Industrie Canada	(11) CA 2 326 560 (40) 16.05.2001 (43) 16.05.2001	(13) A1
(12)					
(21)	2 326 560		(51) Int. Cl. 7:	C11D 3/395, C01B 15/00, C11D 7/38, C11D 3/39, C11D 3/40, C11D 7/54	
(22)	16.11.2000				
(30)	199 54 959.1 DE 16.11.1999		(72)	LARSON, BERND (DE). RAEHSE, WILFRIED (DE).	
(71)	HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, Henkelstrasse 67 D-40589, DUSSELDORF, XX (DE).		(74)	SWABEY OGILVY RENAULT	

(54) PARTICULES EN COMPOSES PEROXOS COMPORTANT UN REVETEMENT
(54) COATED PARTICULATE PEROXO COMPOUNDS

(57) Claimed are mono- or multilayer coated particulate peroxy compounds having a core of one or more peroxy compounds and a coating of predominantly inorganic compounds, wherein the core or the coating comprises one or more dyes. The particles are colored and are particularly suitable to be incorporated into solid detergents and cleaners in order to introduce into these a further colored component.



C I P O
CANADIAN INTELLECTUAL
PROPERTY OFFICE

(12)(19)(CA) Demande-Application

(21)(A1) 2,326,560

(22) 2000/11/16

(43) 2001/05/16

(72) RAEHSE, WILFRIED, DE
(72) LARSON, BERND, DE
(71) HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, DE
(51) Int.Cl.⁷ C11D 3/395, C11D 7/54, C11D 3/40, C01B 15/00, C11D 3/39,
C11D 7/38
(30) 1999/11/16 (199 54 959.1) DE
(54) PARTICULES EN COMPOSES PEROXOS COMPORTANT UN
REVETEMENT
(54) COATED PARTICULATE PEROXO COMPOUNDS

(57) Claimed are mono- or multilayer coated particulate peroxy compounds having a core of one or more peroxy compounds and a coating of predominantly inorganic compounds, wherein the core or the coating comprises one or more dyes. The particles are colored and are particularly suitable to be incorporated into solid detergents and cleaners in order to introduce into these a further colored component.



Industrie Canada Industry Canada

Abstract

Claimed are mono- or multilayer coated particulate peroxyo compounds having a core of one or more peroxyo compounds and a coating of predominantly inorganic compounds, wherein the core or the coating comprises one or more dyes. The particles are colored and are particularly suitable to be incorporated into solid detergents and cleaners in order to introduce into these a further colored component.

Coated particulate peroxy compounds

The present invention relates to mono- or multilayer coated particulate peroxy compounds having a core of 5 one or more peroxy compounds and a coating of inorganic salts, and to a process for the preparation of these particulate compounds.

Peroxy compounds, in particular percarbonates and 10 perborates, are used as active oxygen component in detergents, bleaches and cleaners. Because of the inadequate storage stability of, in particular, sodium percarbonate in a warm-damp environment, and in the presence of various detergent and cleaner components, 15 the peroxy compounds, in particular sodium percarbonate, are stabilized against the loss of active oxygen. An essential principle for the stabilization consists in covering the particles of the peroxy compounds with a sheath of components which have a 20 stabilizing action.

DE-A-24 17 572 discloses a process for the stabilization of particulate peroxy compounds, in particular the persalts of alkali metals, by forming a 25 coating layer. The coating substance used is a mixture formed by crystallization of a sodium carbonate with other mineral salts, such as sodium dicarbonate and/or sodium sulfate.

30 DE-A 26 51 442 discloses sodium percarbonate particles which consist of a sodium percarbonate core and a coating of dehydrated sodium perborate.

European patents or patent applications 35 EP 0 567 140 B1, EP 0 592 969 B1, EP 0 623 553 A1, EP 0 675 851 B1 and EP 0 710 215 B1 describe further coated sodium percarbonate particles which comprise various coating systems of inorganic substances, in

particular of silicates, alkali metal salts and alkaline earth metal salts.

Although the improvement of the washing and cleaning activity of the compositions, and the storage stability thereof is a main aim in developing new detergents and cleaners, the esthetic aspects are also increasingly being taken into consideration. The compositions, which are, for example, in powder form or in compacted form, as granulates or extrudates or else as moldings (tablets), are often manufactured as multicolored products.

Particularly in the case of the preparation of granular detergents and cleaners, the peroxy compounds are mixed in as additive components to the other constituents as finished granulates. For components which can be mixed in, it is particularly desirable if, as a result, a further colored constituent can be incorporated into the detergent and cleaner. However, the known particulate peroxy compounds are hitherto known only in their own color.

Accordingly, the object of the present invention was to provide colored mono- or multilayer coated particulate peroxy compounds which are suitable as colored additive component for particulate detergents and cleaners.

Surprisingly, it has been found that if, during the preparation of particulate peroxy compounds which are stabilized by one or more coatings, these coatings are provided with one or more dyes, or the ready-coated particles are treated with a dye [lacuna].

Accordingly, the present invention provides mono- or multilayer coated particulate peroxy compounds having a core of one or more peroxy compounds and a coating of

predominantly inorganic compounds, wherein the core and/or the coating comprise one or more dyes.

Suitable coloring agents which may be present in the
5 particulate peroxy compounds according to the invention or may be applied thereto are all coloring agents which can be destroyed oxidatively in the washing process, and mixtures thereof with suitable blue dyes, so-called blue toners.

10

Preferred dyes have high storage stability and are insensitive toward the ingredients of the composition and toward light and do not have marked substantivity toward the treated substrates, such as textile fibers
15 or parts of dishes, in order not to color these substrates.

Dyes which are soluble or suspendable in water or organic substances which are liquid at room temperature
20 have proven particularly suitable.

Suitable are, for example, anionic coloring agents, e.g. anionic nitroso dyes. One possible coloring agent is, for example, naphthol green (Colour Index (CI) Part
25 1: Acid Green 1; Part 2: 10020), which is available as a commercial product, for example as Basacid® Green 970 from BASF, Ludwigshafen, and mixtures thereof with suitable blue dyes. Further coloring agents which may be used are Pigmosol® Blue 6900 (CI 74160), Pigmosol®
30 Green 8730 (CI 74260), Basonyl® Red 545 FL (CI 45170), Sandolan® Rhodamin EB400 (CI 45100), Basacid® Yellow 094 (CI 47005), Sicovit® Patent Blue 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183), Pigment Blue 15 (CI 74160), Supranol® Blue GLW (CAS 12219-32-8, CI Acid Blue 221), Nylosan® Yellow N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) and/or Sandolan® Blue (CI Acid Blue 182, CAS 12219-26-0).

Further suitable coloring agents are Ponceau 4R (CAS No. 2611-82-7, CI 16255), Allura Red 40 (CAS No. 25956-17-6, CI 16035), Aluminum Red RLW (CI Mordant Red 83), Supranol® Red GW (CAS No. 61901-44-8), Basantol® Red 310 (CAS No. 61951-36-8), Basacid® Green 970 (CAS No. 19381-50-1), Supranol® Green 6 GW (anthraquinone dye preparation with Acid Green 81), Supranol® Green BW (anthraquinone dye preparation with Acid Green 84), Ultramarine Blue 6394 (CAS No. 57455-37-5, CI 77007), Acid Yellow 17 (CAS No. 6359-98-4, CI 18965), Acid Yellow 23 (CAS No. 1934-21-0, CI 19140).

Likewise suitable are the substances known as optical brighteners whose use is known in detergents and cleaners from the prior art. These are organic dyes which convert part of the nonvisible UV radiation of sunlight into longer-wavelength blue light. They essentially comprise five structural groups, the stilbene group, the diphenylstilbene group, the coumarin group, the quinoline group, the diphenylpyrazoline group and the group of the combination of benzoxazole or benzimidazole with conjugated systems. An overview of common brighteners is given, for example, in G. Jakobi, A. Löhr "Detergents and Textile Washing", VCH-Verlag, Weinheim, 1987, pages 94 to 100. Suitable are e.g. salts of 4,4'-bis[(4-anilino-6-morpholino-s-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid or similarly constructed compounds which, instead of the morpholino group, have a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group. It is also possible for brighteners of the substituted diphenylstyryl type to be present, e.g. the alkali metal salts of 4,4'-bis(2-sulfostyryl)diphenyl, or 4,4'-bis(4-chloro-3-sulfostyryl)diphenyl, or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)diphenyl.

The dyes are preferably applied in an amount of from 0.001 to 0.15% by weight, calculated as dry solid and based on the weight of the coating.

5 Examples of peroxy compounds are, in particular, the percarbonates, perborates, perpyrophosphates, pertripolyphosphates, persilicates, peroxymonosulfates and any mixtures thereof. These compounds are usually in the form of the alkali metal salts, in particular as
10 sodium salts. Further suitable peroxy compounds are citrate perhydrate, and H₂O₂-supplying peracidic salts or peracids, such as perbenzoates, peroxyphthalates, diperazelaic acid, phthaloiminoperacid or diperdecanedioic acid. A particularly preferred peroxy
15 compound is sodium percarbonate.

The coating materials may be chosen from any inorganic substances which are suitable to be applied to the particulate peroxy compounds and have a stabilizing
20 action on the peroxy compounds, i.e. do not significantly reduce their active oxygen content. Examples of coating materials are alkali metal salts, in particular sodium halides, sodium carbonates, such as sodium hydrogencarbonate and sodium carbonate, the
25 sulfates, alkaline earth metal salts, such as magnesium salts, in particular magnesium sulfate, alkali metal silicates, in particular sodium orthosilicate, sodium metasilicate and water glass, boron compounds, such a boric acid, borates and dehydrated perborate, and any
30 mixtures of the abovementioned compounds. Specific examples of coating materials are a cocrystallisate of sodium carbonate with other mineral salts, such as sodium bicarbonate and/or sodium sulfate, a mixture of dehydrated sodium perborate and a sodium silicate, such
35 as sodium metasilicate, sodium disilicate and sodium orthosilicate, a mixture of boric acid or borates and alkali metal compounds, such as sodium sulfate, potassium sulfate, magnesium sulfate and calcium

sulfate, a mixture of sodium carbonate and sodium chloride which forms from a mother liquor, as is produced during the preparation of sodium percarbonate by reaction of an aqueous solution or suspension of 5 sodium carbonate with a hydrogen peroxide solution in the presence of quantities of sodium chloride which are sufficient for salting out, and optionally customary auxiliaries, an aqueous solution of boric acid in an alkali metal metasilicate, a mixture of an aqueous 10 silicate solution and a mixed solution of magnesium sulfate, alkali metal sulfate and alkali metal bicarbonate, and a mixture of sodium carbonate and a magnesium compound, such as magnesium sulfate, magnesium chloride or a magnesium carboxylate of a 15 C₁-C₄-carboxylic acid.

The coating is usually applied in an amount of from 0.5 to 20% by weight, based on the peroxy compound.

20 The coating can additionally comprise auxiliaries, i.e. substances which improve the stability of the peroxy compounds or their processability or the melts. Examples of auxiliaries of sodium polyphosphates, 25 sodium carboxylates, sodium silicates, phosphonic acids and salts thereof.

The coating can be mono- or multilayer. If the coating 30 consists of one layer, then it may include one or more of the abovementioned coating materials. If the coating consists of two or more layers, then each coat can 35 consist of different coating materials. Both in the case of the monolayer and the multilayer coating, the coating substances can be chosen as desired depending on the desired stabilizer effect on the peroxy compound. Where appropriate, additional stabilizers may also be added.

The dyes may be introduced or applied (in)to the particulate peroxy compound or be incorporated into the coating layer in any manner. For example, it is possible to add the dye directly during the preparation 5 of the peroxy compound, provided it does not adversely effect the stability and the preparation process, or to apply the dye as a separate layer either directly to the peroxy compound or to the applied coating layer. In a preferred embodiment, the dye is introduced into the 10 coating and is therefore a constituent of this coating.

In a particularly preferred embodiment of the present invention, the particulate peroxy compounds according to the invention have a two layer coating, where, 15 firstly, a coating is applied in an amount such that this first layer comprises 20 to 70% of the total coating and, subsequently, a second layer is applied which comprises the dyes and optionally further substances, in particular organic compounds, for 20 enhancing the color intensity.

Examples of color enhancers which may be mentioned are glycerol, glycerides, nonionic surfactants, in particular hydrophobic nonionic surfactants, fatty 25 alcohols, fatty acid esters, fats, oils, waxes, perfume oils, etc.

The coated particulate peroxy compounds according to the invention are prepared by processes known from the 30 prior art by treating the particulate peroxy compounds in a customary manner with the coating substances, which usually represents an aqueous solution or suspension of the constituents of these substances, and then drying them. Here, it is possible, for example, to 35 mix the particles of the peroxy compounds with the aqueous coating material in a mixer and then to dry the particles treated in this way, or, in a likewise known manner, the aqueous coating composition can be sprayed

onto the particles in a fluidized-bed dryer through which warm air passes, drying taking place simultaneously.

- 5 To prepare the particulate peroxy compounds coated according to the invention in a fluidized bed, the particles to be coated which are in the fluidized bed are sprayed with the coating material while maintaining a fluidized-bed temperature of from 30 to 100°C, and
10 are dried simultaneously or subsequently.

If two or more layers are applied, then the aqueous solutions or dispersions of the coated materials are sprayed on successively.

- 15 The colored coated particulate peroxy compounds prepared according to the invention are particularly suitable for further processing in detergents and cleaners, in particular in pulverulent, granular,
20 extruded or tableted compositions.

For use in detergents and cleaners, preference is given to using particulate peroxy compounds which have a spherical shape and a diameter of from 0.8 mm to
25 3.0 mm, in particular from 1.4 to 2.5 mm.

- In a further preferred embodiment of the present invention, coated peroxy compounds are used which have two variable particle size distributions, the first
30 particle size distribution having an average particle diameter from 0.8 mm to 1.4 mm, and the second particle size distribution being from 1.5 to 2.5 mm.

- Also provided are detergents and cleaners comprising
35 surfactants, bleaches and optionally further customary ingredients, wherein, as bleaches, the above-described mono- or multilayer coated particulate peroxy compounds

having a core of one or more peroxy compounds and a coating of inorganic compounds are present.

In such compositions, the particulate peroxy compounds
5 are present in amounts up to 30% by weight, based on
the finished composition, preferably from 1 to 30% by
weight and in particular from 3 to 18% by weight. They
introduce a further colored component into the
composition, which significantly increases the overall
10 esthetic impression.

The compositions according to the invention comprise
surfactants, e.g. nonionic, anionic and amphoteric
15 surfactants, and bleaches, and optionally further
customary ingredients.

The nonionic surfactants used are preferably
alkoxylated, advantageously ethoxylated, in particular
primary alcohols having preferably 8 to 18 carbon atoms
20 and on average 1 to 12 mol of ethylene oxide (EO) per
mole of alcohol, in which the alcohol radical may be
linear or, preferably, methyl-branched in the
2-position, or may contain linear and methyl-branched
radicals in the mixture, as customarily are present in
25 oxo alcohol radicals. However, particular preference is
given to alcohol ethoxylates containing linear radicals
from alcohols of native origin having 12 to 18 carbon
atoms, e.g. from coconut, palm, tallow fatty or oleyl
alcohol, and on average 2 to 8 EO per mole of alcohol.
30 Preferred ethoxylated alcohols include, for example,
 C_{12-14} -alcohols with 3 EO or 4 EO, C_{9-11} -alcohol with
7 EO, C_{13-15} -alcohols with 3 EO, 5 EO, 7 EO or 8 EO,
 C_{12-18} -alcohols with 3 EO, 5 EO or 7 EO and mixtures
thereof, such as mixtures of C_{12-14} -alcohol with 3 EO and
35 C_{12-18} -alcohol with 5 EO. The degrees of ethoxylation
given are statistical average values which, for a
specific product, may be an integer or a fraction.
Preferred alcohol ethoxylates have a narrowed homologue

distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants it is also possible to use fatty alcohols having more than 12 EO. Examples thereof are tallow fatty alcohol with 14 EO,
5 25 EO, 30 EO or 40 EO.

A further class of preferred nonionic surfactants, which are used either as the sole nonionic surfactant or in combination with other nonionic surfactants, are
10 alkoxylated, preferably ethoxylated or ethoxylated and propoxylated fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, in particular fatty acid methyl esters, as are described, for example, in the Japanese patent application
15 JP 58/217598, or which are preferably prepared by the process described in international patent application WO-A-90/13533.

A further class of nonionic surfactants which can
20 advantageously be used are the alkyl polyglycosides (APG). Alkyl polyglycosides which can be used satisfy the general formula $RO(G)_z$, in which R is a linear or branched, in particular methyl-branched in the 2 position, saturated or unsaturated aliphatic radical
25 having 8 to 22, preferably 12 to 18, carbon atoms, and G is the symbol which stands for a glucose unit having 5 or 6 carbon atoms, preferably for glucose. The degree of glycosylation z is here between 1.0 and 4.0, preferably between 1.0 and 2.0 and in particular
30 between 1.1 and 1.4. Preference is given to using linear alkyl polyglucosides, i.e. alkyl polyglycosides in which the polyglycosyl radical is a glucose radical and the alkyl radical is an n-alkyl radical.

35 Also, nonionic surfactants of the amine oxide type, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamides may be suitable. The amount of

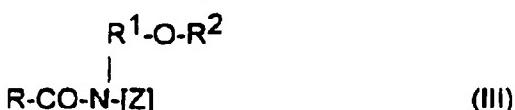
these nonionic surfactants is preferably no more than that of the ethoxylated fatty alcohols, in particular no more than half thereof.

- 5 Further suitable surfactants are polyhydroxy fatty acid amides of the formula (II)



in which RCO is an aliphatic acyl radical having 6 to
 10 carbon atoms, R^1 is hydrogen, an alkyl or hydroxy-alkyl radical having 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances
 15 which can usually be obtained by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

20 The group of polyhydroxy fatty acid amides also includes compounds of the formula III



25 in which R is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R^1 is a linear, branched or cyclic alkyl radical or an aryl radical having 2 to 8 carbon atoms, and R^2 is a linear, branched or cyclic alkyl radical or an aryl radical or
 30 an oxy-alkyl radical having 1 to 8 carbon atoms, where C₁₋₄-alkyl or phenyl radicals are preferred and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or

alkoxylated, preferably ethoxylated or propoxylated, derivatives of this radical.

[Z] is preferably obtained by reductive amination of a
5 reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds can then be converted into the desired polyhydroxy fatty acid amides, for example in accordance with the teaching of the
10 international patent application WO-A-95/07331, by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst.

The surfactants are present in the cleaners or
15 detergents according to the invention in a total amount of, preferably, from 5% by weight to 50% by weight, in particular from 8% by weight to 30% by weight, based on the finished composition.

20 The anionic surfactants used are, for example, those of the sulfonate and sulfate type. Suitable surfactants of the sulfonate type are, preferably, C₉₋₁₃-alkylbenzene-sulfonates, olefinsulfonates, i.e. mixtures of alkene- and hydroxyalkanesulfonates, and disulfonates, as
25 obtained, for example, from C₁₂₋₁₈-monoolefins having a terminal or internal double bond by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Also suitable are alkanesulfonates, which are obtained from
30 C₁₂₋₁₈-alkanes, for example by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization. Also suitable are the esters of α -sulfo fatty acids (ester sulfonates), e.g. the α -sulfonated methyl esters of hydrogenated coconut, palm kernel or
35 tallow fatty acids.

Further suitable anionic surfactants are sulfated fatty acid glycerol esters. Fatty acid glycerol esters means

the mono-, di- and triesters, and mixtures thereof, as are obtained during the preparation by esterification of a monoglycerol with 1 to 3 mol of fatty acid or during the transesterification of triglycerides with 5 0.3 to 2 mol of glycerol. Preferred sulfated fatty acid glycerol esters are the sulfation products of saturated fatty acids having 6 to 22 carbon atoms, for example of caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or 10 behenic acid.

Preferred alk(en)ylsulfates are the alkali metal, and in particular sodium, salts of sulfuric half-esters of C₁₂-C₁₈-fatty alcohols, for example from coconut fatty 15 alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of C₁₀-C₂₀-oxo alcohols and those half-esters of secondary alcohols of these chain lengths. Also preferred are alk(en)ylsulfates of said chain length which contain a synthetic straight-chain 20 alkyl radical prepared on the basis of petroleum, which have degradation behavior analogous to that of the appropriate compounds based on fatty chemical raw materials. From a washing-performance viewpoint, the C₁₂-C₁₆-alkylsulfates and C₁₂-C₁₅-alkylsulfates, and 25 C₁₄-C₁₅-alkylsulfates are preferred. 2,3-Alkylsulfates, which are prepared, for example, according to US patent specification 3,234,258 or 5,075,041 and can be obtained as commercial products from Shell Oil Company under the name DAN®, are also suitable anionic 30 surfactants.

The sulfuric monoesters of the straight-chain or branched C₇-C₂₁-alcohols ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl-branched C₉-C₁₁-alcohols 35 having, on average, 3.5 mol of ethylene oxide (EO) or C₁₂-C₁₈-fatty alcohols having from 1 to 4 EO, are also suitable. Because of their high foaming behavior, they are only used in surfactant compositions or cleaners in

relatively small amounts, for example in amounts of from 1 to 5% by weight.

Further suitable anionic surfactants are also the salts
5 of alkylsulfosuccinic acid, which are also referred to as sulfosuccinates or as sulfosuccinic esters, and which represent monoesters and/or diesters of sulfo-
succinic acid with alcohols, preferably fatty alcohols and, in particular, ethoxylated fatty alcohols.
10 Preferred sulfosuccinates contain C₈₋₁₈-fatty alcohol radicals or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol radical derived from ethoxylated fatty alcohols which, viewed per se, are nonionic surfactants (see below for description).
15 Here, sulfosuccinates whose fatty alcohol radicals are derived from ethoxylated fatty alcohols with a narrowed homologue distribution are in turn particularly preferred. Likewise, it is also possible to use alk(en)ylsuccinic acid having, preferably, 8 to 18
20 carbon atoms in the alk(en)yl chain or salts thereof.

Suitable further anionic surfactants are, in particular, soaps. Saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid,
25 stearic acid, hydrogenated erucic acid and behenic acid, and soap mixtures derived, in particular, from natural fatty acids, e.g. coconut, palm kernel or tallow fatty acids, are suitable.

30 The anionic surfactants, including the soaps, can be present in the form of their sodium, potassium or ammonium salts, and as soluble salts of organic bases, such as mono-, di- or triethanolamine. The anionic surfactants are preferably in the form of their sodium
35 or potassium salts, in particular in the form of the sodium salts.

In order, in the case of washing at temperatures of 60°C and below, and in particular during laundry pretreatment, to achieve an improved bleaching action, bleach activators can be incorporated into the detergent and cleaner moldings. Bleach activators which may be used are compounds which, under perhydrolysis conditions, produce aliphatic peroxocarboxylic acids having, preferably, 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or optionally substituted 5 perbenzoic acid. Suitable substances are those which carry O- and/or N-acyl groups of said carbon number, and/or optionally substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, 10 in particular tetraacetylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), 15 acylated glycolurils, in particular 1,3,4,6-tetra-acetylglycoluril (TAGU), N-acylimides, in particular N-nanoylsuccinimide (NOSI), acylated phenolsulfonates, in particular n-nanoyl or 20 isonanoyloxybenzenesulfonate (n- or iso-NOBS), acylated hydroxycarboxylic acids, such as triethyl O-acetylcitrate (TEOC), carboxylic anhydrides, in particular phthalic anhydride, isatoic anhydride and/or 25 succinic anhydride, carboxamides, such as N-methyldiacetamide, glycolide, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate, isopropenyl acetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from the 30 German patent applications DE 196 16 693 and DE 196 16 767, and acetylated sorbitol and mannitol and/or mixtures thereof (SORMAN) described in European patent application EP 0 525 239, acylated sugar derivatives, in particular pentaacetylglucose (PAG), 35 pentaacetylfructose, tetraacetylxylose and octaacetylactose, and acetylated, optionally N-alkylated glucamine or gluconolactone, triazole or triazole derivatives and/or particulate caprolactams

and/or caprolactam derivatives, preferably N-acylated lactams, for example N-benzoylcaprolactam and N-acetylcaprolactam, which are known from international patent applications WO-A-94/27970, WO-A-94/28102, 5 WO-A-94/28103, WO-A-95/00626, WO-A-95/14759 and WO-A-95/17498. The hydrophilically substituted acylacetals known from German patent application DE-A-196 16 769, and the acyllactams described in German patent application DE-A-196 16 770 and 10 international patent application WO-A-95/14075 are likewise used with preference. It is also possible to use the combinations of conventional bleach activators known from German patent application DE-A-44 43 177. It is also possible to use nitrile derivatives, such as 15 cyanopyridines, nitrile quats and/or cyanamide derivatives. Preferred bleach activators are sodium 4-(octanoyloxy)benzenesulfonate, undecenoyloxybenzenesulfonate (UDOBS), sodium dodecanoyloxybenzenesulfonate (DOBS), 20 decanoyloxybenzoic acid (DOBA, OBC 10) and/or dodecanoyloxybenzenesulfonate (OBS 12), and N-methylmorpholinumacetonitrile (MMA). Such bleach activators may be present in the customary quantitative range from 0.01 to 20% by weight, preferably in amounts 25 of from 0.1 to 15% by weight, in particular 1% by weight to 10% by weight, based on the total composition.

In addition to the conventional bleach activators, or 30 instead of them, so-called bleach catalysts may also be present. These substances are bleach-boosting transition metal salts or transition metal complexes, such as, for example, Mn, Fe, Co, Ru or Mo salen complexes or carbonyl complexes. Mn, Fe, Co, Ru, Mo, 35 Ti, V and Cu complexes with N-containing tripod ligands, and Co, Fe, Cu and Ru ammine complexes are also suitable as bleach catalysts, preference being

given to using those compounds described in DE 197 09 284 A1.

The compositions according to the invention usually 5 comprise one or more builders, in particular zeolites, silicates, carbonates, organic cobuilders and, where there is no ecological prejudice against their use, also the phosphates. The latter are preferred builders to be used in particular in detergent tablets for 10 machine dishwashing.

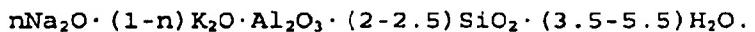
Suitable crystalline, layered sodium silicates have the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot\text{H}_2\text{O}$, where M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number 15 from 0 to 20, and preferred values for x are 2, 3 or 4. Preferred crystalline phyllosilicates of the given formula are those in which M is sodium and x assumes the value 2 or 3. In particular, both β - and δ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5\cdot y\text{H}_2\text{O}$ are preferred.

It is also possible to use amorphous sodium silicates having an $\text{Na}_2\text{O}:\text{SiO}_2$ modulus of from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8 and in particular from 1:2 to 1:2.6, which have delayed solubility and secondary 25 detergency properties. The dissolution delay relative to conventional amorphous sodium silicates can have been induced in various ways, for example by surface treatment, compounding, compaction/compression or by overdrying. Within the scope of this invention, the term "amorphous" also means "X-ray-amorphous". This 30 means that in X-ray diffraction experiments, the silicates do not give sharp X-ray reflections typical of crystalline substances, but, at best, one or more maxima of the scattered X-ray radiation, which have a width of several degree units of the angle of diffraction. However, it is very probable that 35 particularly good builder properties may result if, in electron diffraction experiments, the silicate

particles give poorly defined or even sharp diffraction maxima. This is to be interpreted to the effect that the products have microcrystalline regions of size 10 to a few hundred nm, values up to a maximum of 50 nm 5 and in particular up to a maximum of 20 nm being preferred. Particular preference is given to compressed/compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates.

10

The finely crystalline, synthetic zeolite which contains bonded water which is used is preferably zeolite A and/or P. Zeolite P is particularly preferably Zeolith MAP® (commercial product from Crosfield). Also suitable, however, are zeolite X and mixtures of A, X and/or P. A zeolite which is commercially available and can be used with preference within the scope of the present invention is, for example, also a cocrystallise of zeolite X and 20 zeolite A (about 80% by weight of zeolite X), which is sold by CONDEA Augusta S.p.A. under the trade name VEGOBOND AX® and can be described by the formula



25

Suitable zeolites have an average particle size of less than 10 µm (volume distribution; measurement method: Coulter counter) and preferably contain 18 to 22% by weight, in particular 20 to 22% by weight, of bonded 30 water.

It is of course also possible to use the generally known phosphates as builder substances, provided such a use should not be avoided for ecological reasons. Of 35 the large number of commercially available phosphates, the alkali metal phosphates, particularly preferably pentasodium or pentapotassium triphosphate (sodium or

potassium tripolyphosphate), are of the greatest importance in the detergents and cleaners industry.

Alkali metal phosphates is the collective term for the
5 alkali metal (in particular sodium and potassium) salts
of the various phosphoric acids, among which
metaphosphoric acids (HPO_3)_n and orthophosphoric acid
 H_3PO_4 , in addition to higher molecular weight
representatives, may be differentiated. The phosphates
10 combine a number of advantages: they act as alkali
carriers, prevent limescale deposits on machine
components, and lime incrustations in fabrics, and
additionally contribute to the cleaning performance.

15 Sodium dihydrogenphosphate, NaH_2PO_4 , exists as the
dihydrate (density 1.91 gcm⁻³, melting point 60°) and as
the monohydrate (density 2.04 gcm⁻³). Both salts are
white powders which are very readily soluble in water,
which lose the water of crystallization upon heating
20 and undergo conversion at 200°C into the weakly acidic
diphosphate (disodium hydrogendiphosphate, $Na_2H_2P_2O_7$),
at a higher temperature into sodium trimetaphosphate
($Na_3P_3O_9$) and Maddrell's salt (see below). NaH_2PO_4 is
acidic; it is formed if phosphoric acid is adjusted to
25 a pH of 4.5 using sodium hydroxide solution and the
slurry is sprayed. Potassium dihydrogenphosphate
(primary or monobasic potassium phosphate, potassium
biphosphate, PDP), KH_2PO_4 , is a white salt of density
2.33 gcm⁻³, has a melting point of 253° [decomposition
30 with the formation of potassium polyphosphate (KPO_3)_n]
and is readily soluble in water.

Disodium hydrogenphosphate (secondary sodium
phosphate), Na_2HPO_4 , is a colorless, very readily water-
35 soluble crystalline salt. It exists in anhydrous form
and with 2 mol of water (density 2.066 gcm⁻³, water loss
at 95°), 7 mol of water (density 1.68 gcm⁻³, melting
point 48° with loss of 5 H₂O) and 12 mol of water

(density 1.52 gcm⁻³, melting point 35° with loss of 5 H₂O), becomes anhydrous at 100° and converts to the diphosphate Na₄P₂O₇, upon more severe heating. Disodium hydrogenphosphate is prepared by neutralizing phosphoric acid with soda solution using phenol phthalein as indicator. Dipotassium hydrogenphosphate (secondary or dibasic potassium phosphate), K₂HPO₄, is an amorphous white salt which is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate, Na₃PO₄, are colorless crystals which as the dodecahydrate have a density of 1.62 gcm⁻³ and a melting point of 73-76°C (decomposition), as the decahydrate (corresponding to 19-20% of P₂O₅) have a melting point of 100°C and in anhydrous form (corresponding to 39-40% of P₂O₅) have a density of 2.536 gcm⁻³. Trisodium phosphate is readily soluble in water with an alkaline reaction and is prepared by evaporative concentration of a solution of exactly 1 mol of disodium phosphate and 1 mol of NaOH. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K₃PO₄, is a white, deliquescent, granular powder of density 2.56 gcm⁻³, has a melting point of 1340° and is readily soluble in water with an alkaline reaction. It is produced, for example, when Thomas slag is heated with charcoal and potassium sulfate. Despite the relatively high price, the more readily soluble and therefore highly effective potassium phosphates are often preferred in the cleaners industry over corresponding sodium compounds.

Tetrasodium diphosphate (sodium pyrophosphate), Na₄P₂O₇, exists in anhydrous form (density 2.534 gcm⁻³, melting point 988°, 880° also reported) and as the decahydrate (density 1.815-1.836 gcm⁻³, melting point 94° with loss of water). Both substances are colorless crystals which are soluble in water with an alkaline reaction. Na₄P₂O₇ is formed when disodium phosphate is heated at >200° or

by reacting phosphoric acid with soda in the stoichiometric ratio and dewatering the solution by spraying. The dehydrate complexes heavy metal salts and water hardness constituents and therefore reduces
5 the hardness of the water. Potassium diphosphate (potassium pyrophosphate), $K_4P_2O_7$, exists in the form of the trihydrate and is a colorless, hygroscopic powder with a density of 2.33 g cm^{-3} which is soluble in water, the pH of the 1% strength solution at 25° being 10.4.

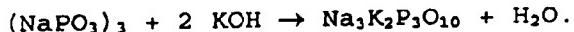
10

Condensation of the NaH_2PO_4 or of the KH_2PO_4 gives rise to higher molecular weight sodium and potassium phosphates, among which it is possible to differentiate between cyclic representatives, the sodium and potassium metaphosphates and catenated types, the sodium and potassium polyphosphates. For the latter, in particular, a large number of names are in use: fused or calcined phosphates, Graham's salt, Kurrol's and Maddrell's salt. All higher sodium and potassium phosphates are referred to collectively as condensed phosphates.

15

The industrially important pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate), is a nonhygroscopic, white, water-soluble salt which is anhydrous or crystallizes with 6 H_2O and has the general formula $NaO-[P(O)(ONA)-O]_n-Na$ where $n=3$. About 17 g of the anhydrous salt dissolve in 100 g of water at room temperature, about 20 g dissolve at $60^\circ C$, and about
20 30 g dissolve at 100° ; after heating the solution for 2 hours at 100° , about 8% orthophosphate and 15% diphosphate are produced by hydrolysis. In the case of the preparation of pentasodium triphosphate, phosphoric acid is reacted with soda solution or sodium hydroxide solution in the stoichiometric ratio and the solution is dewatered by spraying. Similarly to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves many insoluble metal compounds (including
35

lime soaps, etc.). Pentapotassium triphosphate, $K_5P_3O_{10}$ (potassium tripolyphosphate), is commercially available, for example, in the form of a 50% strength by weight solution (> 23% P_2O_5 , 25% K_2O). The potassium polyphosphates are widely used in the detergents and cleaners industry. There also exist sodium potassium tripolyphosphates, which can likewise be used within the scope of the present invention. These form, for example, when sodium trimetaphosphate is hydrolyzed 10 with KOH:



These can be used in accordance with the invention in 15 exactly the same way as sodium tripolyphosphate, potassium tripolyphosphate or mixtures of the two; according to the invention, it is also possible to use mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate 20 or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphosphate.

Organic cobuilders which may be used in the 25 compositions according to the invention are, in particular, polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, further organic cobuilders (see below), and phosphonates. These classes of substance are described 30 below.

Organic builder substances which can be used are, for example, the polycarboxylic acids usable in the form of their sodium salts, the term polycarboxylic acids 35 meaning carboxylic acids which carry more than one acid function. Examples of these are citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids,

aminocarboxylic acids, nitrilotriacetic acid (NTA), provided such a use is not objectionable on ecological grounds, and mixtures thereof. Preferred salts are the salts of the polycarboxylic acids such as citric acid,
5 adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

The acids per se may also be used. In addition to their builder action, the acids typically also have the
10 property of an acidifying component and thus also serve to establish a lower and milder pH of detergents or cleaners. In this connection, particular mention is made of citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any mixtures thereof.

15 Also suitable as builders are polymeric polycarboxylates; these are, for example, the alkali metal salts of polyacrylic acid or of polymethacrylic acid, for example those having a relative molecular
20 mass of from 500 to 70 000 g/mol.

The molar masses given for polymeric polycarboxylates are, for the purposes of this specification, weight-average molar masses, M_w of the respective acid form,
25 determined fundamentally by means of gel permeation chromatography (GPC) using a UV detector. The measurement was made against an external polyacrylic acid standard which, owing to its structural similarity to the polymers under investigation, provides realistic
30 molecular weight values. These figures differ considerably from the molecular weight values obtained using polystyrenesulfonic acids as the standard. The molar masses measured against polystyrenesulfonic acids are usually considerably higher than the molar masses
35 given in this specification.

Suitable polymers are, in particular, polyacrylates which preferably have a molecular mass of from 2000 to

20 000 g/mol. Owing to their superior solubility, preference in this group may be given in turn to the short-chain polyacrylates which have molar masses of from 2000 to 10 000 g/mol and particularly preferably 5 from 3000 to 5000 g/mol.

Also suitable are copolymeric polycarboxylates, in particular those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic 10 acid. Copolymers which have proven to be particularly suitable are those of acrylic acid with maleic acid which contain from 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid. Their relative molecular mass, based on free acids, is generally 2000 15 to 70 000 g/mol, preferably 20 000 to 50 000 g/mol and in particular 30 000 to 40 000 g/mol.

The (co)polymeric polycarboxylates can either be used as powders or as aqueous solutions. The (co)polymeric 20 polycarboxylate content of the composition is preferably 0.5 to 20% by weight, in particular 3 to 10% by weight.

To improve the solubility in water, the polymers can 25 also contain allylsulfonic acids, such as, for example, allyloxybenzenesulfonic acid and methallylsulfonic acid, as monomer.

Particular preference is also given to biodegradable 30 polymers of more than two different monomer units, for example those which contain, as monomers, salts of acrylic acid and of maleic acid, and vinyl alcohol or vinyl alcohol derivatives, or those which contain, as monomers, salts of acrylic acid and of 2-alkylallyl-35 sulfonic acid, and sugar derivatives.

Further preferred copolymers are those which preferably have, as monomers, acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate.

5 Further preferred builder substances which may be mentioned are also polymeric aminodicarboxylic acids, their salts or their precursor substances. Particular preference is given to polyaspartic acids or salts and derivatives thereof.

10

Further suitable builder substances are polyacetals, which can be obtained by reacting dialdehydes with polyolcarboxylic acids which have 5 to 7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals

15

are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyolcarboxylic acids such as gluconic acid and/or glucoheptonic acid.

20

Further suitable organic builder substances are dextrins, examples being oligomers or polymers of carbohydrates, which can be obtained by partial hydrolysis of starches. The hydrolysis can be carried out by customary processes, for example acid-catalyzed or enzyme-catalyzed processes. The hydrolysis products

25

preferably have an average molar mass in the range from 400 to 500 000 g/mol. Preference is given here to a polysaccharide having a dextrose equivalent (DE) in the range from 0.5 to 40, in particular from 2 to 30, where

30

DE is a common measure of the reducing effect of a polysaccharide compared with dextrose, which has a DE of 100. It is also possible to use both maltodextrins having a DE between 3 and 20 and dried glucose syrups having a DE between 20 and 37, and also so-called yellow dextrins and white dextrins with higher molar masses in the range from 2000 to 30 000 g/mol.

35

The oxidized derivatives of such dextrans are their reaction products with oxidizing agents which are able to oxidize at least one alcohol function of the saccharide ring to the carboxylic acid function. An 5 oxidized oligosaccharide is likewise suitable, a product oxidized on the C₆ of the saccharide ring being particularly advantageous.

Oxydisuccinates and other derivatives of disuccinates, 10 preferably ethylenediamine disuccinate, are also further suitable cobuilders. Here, ethylenediamine N,N'-disuccinate (EDDS) is preferably used in the form of its sodium or magnesium salts. In this connection further preference is also given to glycerol 15 disuccinates and glycerol trisuccinates. Suitable use amounts in zeolite-containing and/or silicate-containing formulations are 3 to 15% by weight.

Further organic cobuilders which can be used are, for 20 example, acetylated hydroxycarboxylic acids or salts thereof, which may also be present in lactone form and which contain at least 4 carbon atoms and at least one hydroxyl group and at most two acid groups.

25 A further class of substance having cobuilder properties is the phosphonates. These are, in particular, hydroxyalkane- and aminoalkanephosphonates. Among the hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as 30 a cobuilder. It is preferably used as sodium salt, the disodium salt being neutral and the tetrasodium salt being alkaline (pH 9). Suitable aminoalkanephosphonates are preferably ethylenediaminetetramethylenephosphonate (EDTMP), diethylenetriaminepentamethylenephosphonate 35 (DTPMP) and higher homologues thereof. They are preferably used in the form of the neutral sodium salts, e.g. as the hexasodium salt of EDTMP or as the hepta- and octasodium salt of DTPMP. Here, preference

is given to using HEDP as builder from the class of phosphonates. In addition, the aminoalkanephosphonates have a marked heavy metal-binding capacity. Accordingly, particularly if the compositions also 5 contain bleaches, it may be preferable to use aminoalkanephosphonates, in particular DTPMP, or mixtures of said phosphonates.

Moreover, all compounds which are able to form 10 complexes with alkaline earth metal ions can be used as cobuilders.

The detergent and cleaner according to the invention can comprise, as further customary ingredients, in 15 particular enzymes, sequestering agents, electrolytes, pH regulators and further auxiliaries, such as optical brighteners, antiredeposition agents, color transfer inhibitors, foam regulators, additional bleach activators, dyes and fragrances.

20 Suitable enzymes which can be used in the compositions are those from the class of oxidases, proteases, lipases, cutinases, amylases, pullulanases, cellulases, hemicellulases, xylanases and peroxidases, and mixtures 25 thereof, for example proteases such as BLAP®, Optimase®, Opticlean®, Maxacal®, Maxapem®, Alcalase®, Esperase® and/or Savinase®, Amylases such as Termamyl®, Amylase-LT®, Maxamyl®, Duramyl® and/or Puraffect® OxAm, lipases such as Lipolase®, Lipomax®, Lumafast® and/or 30 Lipozyme®, cellulases such as Celluzyme® and/or Carezyme®. Particularly suitable are enzymatic active ingredients obtained from fungi or bacteria, such as Bacillus subtilis, Bacillus licheniformis, Streptomyces griseus, Humicola Lanuginosa, Humicola 35 insolens, Pseudomonas pseudoalcaligenes or Pseudomonas cepacia. The optionally used enzymes can, as described, for example, in European patent application EP 0 564 476 or in the international patent application

WO 94/23005, be adsorbed to carrier substances and/or embedded in coating substances in order to protect them against premature deactivation. They are preferably present in the surfactant mixtures according to the invention in amounts up to 10% by weight, in particular from 0.2% by weight to 2% by weight, particular preference being given to using enzymes stabilized against oxidative degradation, as known, for example, from international patent applications WO 94/02597, 10 WO 94/02618, WO 94/18314, WO 94/23053 or WO 95/07350.

In addition to the surfactants, bleaches and builders, a large number of compounds may be used in the detergents, mention being made here, by way of example, 15 of foam inhibitors, phosphonates, enzymes, and optical brighteners.

For use in machine washing processes, it may be advantageous to add customary foam inhibitors to the compositions. Suitable foam inhibitors are, for example, soaps of natural or synthetic origin which have a high proportion of C₁₈-C₂₄-fatty acids. Suitable non-surfactant-like foam inhibitors are, for example, organopolysiloxanes and mixtures thereof with microfine, optionally silanized, silica, and paraffins, waxes, microcrystalline waxes and mixtures thereof with silanized silica or bistearylethylenediamide. Mixtures of different foam inhibitors are also used advantageously, e.g. those of silicones, paraffins or waxes. The foam inhibitors, in particular silicone- or paraffin-containing foam inhibitors, are preferably bonded to a granular, water-soluble or dispersible carrier substance. Particular preference is given here to mixtures of paraffins and bistearylethylenediamides.

As salts of polyphosphonic acids, use is preferably made of the neutrally reacting sodium salts of, for example, 1-hydroxyethane-1,1-diphosphonate, diethylene-

triaminepentamethylenephosphonate or ethylenediaminetetramethylenephosphonate in amounts of from 0.1 to 1.5% by weight.

- 5 The compositions according to the invention can comprise derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as optical brighteners. Suitable are e.g. salts of 4,4'-bis(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)stilbene-2,2'-disulfonic acid or similarly structured compounds which have a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Furthermore, brighteners of the substituted diphenylstyryl type may be present, e.g. 10 the alkali metal salts of 4,4'-bis(2-sulfostyryl)diphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)diphenyl, or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)diphenyl. Mixtures of the abovementioned brighteners may also be used.
- 15 20 If the composition according to the invention is used as a so-called universal detergent, it preferably comprises from 3 to 30% by weight of anionic surfactants, 2 to 20% by weight of nonionic surfactants, 10 to 50% by weight of builder materials, 25 5 to 25% by weight of bleaches, 1 to 10% by weight of bleach activators, 0.3 to 3% by weight of enzymes, 0.3 to 8% by weight of cobuilders and 0.1 to 6% by weight of antifoams.

Patent claims

1. A mono- or multilayer coated particulate peroxy compound having a core of one or more peroxy compounds and a coating of predominantly inorganic compounds, wherein the core and/or the coating comprise one or more dyes.
5
2. The coated particulate peroxy compound as claimed in claim 1, wherein the dyes are chosen from the group consisting of anionic nitroso dyes, such as naphthol green (Colour Index (CI) Part 1: Acid Green 1; Part 2: 10020), Pigmosol® Blue 6900 (CI 74160), Pigmosol® Green 8730 (CI 74260), Basonyl® Red 545 FL (CI 45170), Sandolan® Rhodamin EB400 (CI 45100), Basacid® Yellow 094 (CI 47005), Sicovit® Patent Blue 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183),
10 Pigment Blue 15 (CI 74160), Supranol® Blue GLW (CAS 12219-32-8, CI Acid Blue 221), Nylosan® Yellow N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) or Sandolan® Blue (CI Acid Blue 182, CAS 12219-26-0), Ponceau 4R (CAS No. 2611-82-7, CI 16255), Allura Red 40 (CAS No. 25956-17-6, CI 16035), Aluminum Red RLW (CI Mordant Red 83),
15 Supranol® Red GW (CAS No. 61901-44-8), Basantol® Red 310 (CAS No. 61951-36-8), Basacid® Green 970 (CAS No. 19381-50-1), Supranol® Green 6 GW (anthraquinone dye preparation with Acid Green 81), Supranol® Green BW (anthraquinone dye preparation with Acid Green 84), Ultramarine Blue 6394 (CAS No. 57455-37-5, CI 77007), Acid Yellow 17 (CAS No. 6359-98-4, CI 18965), Acid Yellow 23 (CAS No. 1934-21-0, CI 19140), and optical
20 brighteners.
25
3. The coated particulate peroxy compound as claimed in either of claims 1 and 2, wherein the dyes are
30
35

applied in an amount of from 0.001 to 0.15% by weight, calculated as dry solid and based on the weight of the coating.

- 5 4. The coated particulate peroxy compound as claimed in any of claims 1 to 3, wherein the peroxy compound is chosen from percarbonates, perborates, perpyrophosphates, pertripolyphosphates, persilicates, peroxyomonosulfates, citrate perhydrates and H₂O₂-supplying peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloaminoperacid or diperdodecanedioic acid and any mixtures thereof.
- 10
- 15 5. The coated particulate peroxy compound as claimed in claim 4, wherein the peroxy compound is sodium percarbonate.
- 20
- 25 6. The coated particulate peroxy compound as claimed in any of claims 1 to 5, wherein the coating comprises compounds chosen from alkali metal salts, in particular sodium halides, sodium carbonates, such as sodium hydrogencarbonate and sodium carbonate, alkali metal sulfates, alkaline earth metal salts, such as magnesium salts, in particular magnesium sulfate, alkali metal silicates, in particular sodium orthosilicate, sodium metasilicate and water glass, boron compounds, such as boric acid, borates and dehydrated perborates, and any mixtures of the above.
- 30
- 35 7. The coated particulate peroxy compound as claimed in claim 6, wherein the coating materials are chosen from a cocrystallise of sodium carbonate with other mineral salts, such as sodium bicarbonate and/or sodium sulfate, a mixture of dehydrated sodium perborate and a sodium silicate.

such as sodium metasilicate, sodium disilicate and sodium orthosilicate, a mixture of boric acid or borates and alkali metal compounds, such as sodium sulfate, potassium sulfate, magnesium sulfate and calcium sulfate, a mixture of sodium carbonate and sodium chloride which forms from a mother liquor, as is produced during the preparation of sodium percarbonate by reaction of an aqueous solution or suspension of sodium carbonate with a hydrogen peroxide solution in the presence of quantities of sodium chloride which are sufficient for salting out, and optionally customary auxiliaries, an aqueous solution of boric acid in an alkali metal metasilicate, a mixture of an aqueous silicate solution and a mixed solution of magnesium sulfate, alkali metal sulfate and alkali metal bicarbonate, and a mixture of sodium carbonate and a magnesium compound, such as magnesium sulfate, magnesium chloride or a magnesium carboxylate of a C₁-C₄-carboxylic acid.

8. The coated particulate peroxy compound as claimed in any of claims 1 to 7, wherein auxiliaries chosen from sodium polyphosphates, sodium carboxylates, sodium silicates, phosphonic acids and salts thereof are present.
9. The coated particulate peroxy compound as claimed in any of claims 1 to 8, wherein the peroxy compounds have a spherical shape and have a diameter of from 0.8 mm to 3.0 mm, in particular from 1.4 to 2.5 mm.
10. A process for the preparation of mono- or multi-layer coated particulate peroxy compounds as claimed in any of claims 1 to 9, which comprises treating the particulate peroxy compounds with an aqueous solution or dispersion of the coating

substances and drying the particles treated in this way.

11. The process as claimed in claim 10, wherein the
5 coating substances are applied in a fluidized-bed apparatus.
12. A detergent or cleaner comprising surfactants, bleaches and optionally further customary ingredients, wherein, as bleaches, mono- or multilayer coated particulate peroxy compounds having a core of one or more peroxy compounds and a coating of inorganic compounds as claimed in any of claims 1 to 9 are present.
10
13. The composition as claimed in claim 12, which comprises the mono- or multilayer coated particulate peroxy compounds in amounts of from 1 to 30% by weight, in particular from 3 to 18% by weight, based on the finished composition.
15
14. The composition as claimed in either of claims 12 and 13, which is a universal detergent and comprises from 3 to 30% by weight of anionic surfactants, 2 to 20% by weight of nonionic surfactants, 10 to 50% by weight of builder materials, 5 to 25% by weight of bleaches, 1 to 25
- 30 10% by weight of bleach activators, 0.3 to 3% by weight of enzymes, 0.3 to 8% by weight of cobuilders and 0.1 to 6% by weight of antifoams.